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Title: Ionic Liquid-Mediated Biopolymer Extraction from Coffee Fruit

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Abstract: Ionic liquids (ILs) are effective solvents for biomass. Refined cellulose is commonly used; however, recent interest has grown to consider woody and herbaceous biomass, and industrial crop residues like fruit peels. Here we report results on the dissolution and shaping of cotton and coffee fruit (cascara) in 1,8-Diazabicyclo[5.4.0]undec-7-inium acetate ([DBUH][OAc]). Cascara is a high-volume, low-value crop residue that poses an environmental and economic burden in producer countries leading to a high value-proposition if recoverable. Fruit/ionic liquid solutions (0-15% w/w dissolved at 60°C) were characterized with respect to biomass concentration and shaped into fibers and films coagulated in DI water and methanol. Rheology was assessed using parallel plate rheometry. Cotton/IL mixtures formed better fibers compared to cascara-based solutions, which required 2.6x more biomass in solution for viable fiber formation. At 10% loading, fibers could be produced from untreated coffee fruit with diameters ranging from 18-100s of microns. Coffee fruit residues and their precipitated films show that both cellulose and lignin dissolve in pure [DBUH][OAc]. Chemical characterization of cascara and cascara films demonstrates conveyance of high concentrations of lignin and extracts that result in weaker mechanical properties. Further purification of cascara is required for effective use in structural applications.

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/mame.202300145.

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Introduction

Ionic liquids (ILs) are a rising state of the art for both producing and manipulating man-made cellulosic fibers and structures.[1,2] In the last decade, ILs of varying composition have been explored for both cellulose and more generally, biomass dissolution.[2,3] Ionic liquids are highly tunable organic salts noted for negligible vapor pressures, low melting points (<100 ◦C), and good thermal stability (<200 ◦C).[4] As a result, ILs are thought to be "greener" than conventional organic solvents used to produce synthetic cellulosic fibers in either the lyocell or viscose processes.[5,6] ILs can often achieve higher cellulose solubility limits than conventional viscose and lyocell methods, thus possibly making IL-mediated solvation more efficient and cost effective.[7,8]

For this work, the ionic liquid,1,8-Diazabicyclo[5.4.0]undec-7-inium acetate ([DBUH][OAc]) was selected for a number of reasons including ease of synthesis and cost.[9] Previous literature review we compiled[10] suggests that superbase-derived ILs have a higher cellulose solubility per unit cost. **Table 1** presents a selection of ILs and their processing conditions used in the treatment of various biomasses that informed our experimental conditions. Most bench-scale IL solvation work has been done with highly purified cellulose from cotton discards,[11] microcrystalline cellulose,[12,13] and kraft pulp.[14,15] There is also a growing body of research on the dissolution of less pure biomass sources like woody and herbaceous biomasses[16] as well as reclaimed materials.[17,18] Evidence suggests that the inclusion of larger fractions of common lignocellulosic compounds (lignin and hemicellulose) in biomass mixtures tend to decrease the mechanical properties of the produced fibers by interfering with cellulose crystallization.[19] However, in some instances, the presence of hemicellulose and lignin has actually improved the mechanical properties of coprecipitated cellulose fibers over those derived from pure cellulose.[8,20,21]

The selection of biomass for dissolution in the literature has remained generally conservative, focusing primarily on forestry waste, plant stalks, and leafy components like corn stover and bagasse that have low moisture content and often compete as feedstocks for food, biofuel production and compost.[22,23] We propose that there is utility in considering a wider range of industrial agriculture wastes that may have less intrinsic value

Table 1. Literature review of select IL treated biomasses and their applications

Biomass	IL[a]	condition	Solubility	Product	Ref.
Oil palm mesocarp (isolated cellulose)	[EMIM][Cl]	80◦C, 12 hours	100%	electrospun fibers	[33]
Pineapple crown	[2HEA][OAc],[2HEA][OPr],[2HEA][OBt],[2HEA][OPent],[BHEA][OAc], [BHEA][OPr],[BHEA][OBt],[BHEA][OPent],[m-2HEA][OAc],[m-2HEA][OPr],[m-2HEA][OBt],[m-2HEA][OPent]	100◦C, 1 hour	-	delignification and isolation	[34]
Switchgrass	[EMIM][OAc]	120◦C, 2 hours	100%	saccharification	[35]
Cascara	[DIPEA][OAc], [DIPEA][OPr],[DIPEA][OOct][DIPEA][OBen]	80-120◦C, 4 hours	-	lignin isolation	[32]

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Hybrid poplar (autohydrolysis)	[EMIM][OAc]	100°C, to dissolution	100%	drawn fibers	[36]
Birch kraft pulp	[DBNH][OAc]	85°C, 2 hours	-	drawn fibers	[8]
Cotton lint	[AMIM][Cl]	100°C, to dissolution	100%	extruded fibers	[37]

[a]Acronyms - cations: 1-ethyl-3-methylimidazolium ([EMIM]), 2-hydroxyethylammonium ([2HEA]), bis(2-hydroxyethyl)ammonium ([BHEA]), N-methyl-2-hydroxyethylammonium ([m-2HEA]), diisopropylethylammonium ([DIPEA]), 1-allyl-3-methylimidazolium ([AMIM]); anions: chloride ([Cl]), acetate ([OAc]), propionate ([OPr]), butyrate ([OBt]), pentanoate ([OPent]), octanoate ([OOct], benzoate ([OBen])

and a bigger waste footprint.[24-26] For example, leveraging the waste streams of industrial food production such as coffee fruit waste, pineapple leaf and skin, and banana peel could divert millions of tons of biomass annually[27,28] from landfill or agricultural runoff and reincorporate it into a circular economy.

We explored dried coffee fruit residue, called cascara, as a feedstock for biopolymer fibers. Cascara is the outer fruit of the cultivated coffee cherry, which is often discarded during bean isolation and allowed to decompose naturally. Coffee is a particularly low yield product in that as little as 10% of the cultivated mass is actually bean, and ~45% of the dry mass consists of the discarded fruit.[29] Cascara has limited intrinsic value beyond a small market for the dried fruit as a tea-like drink.[30] With both agricultural intensification and increasing global coffee consumption, coffee waste management has become a substantial burden to producer countries.[31] Previously coffee waste products have been investigated for a number of applications including microfibrils,[25] biofuel feedstocks, compost, animal feeds, and stock chemical extraction.[29] The treatment of coffee fruit with IL has also been explored as a means to extract value-added lignin.[32] Herein, the exploration of coffee fruit waste for cellulose extraction was assessed as a proof of concept to leverage unconventional, high-volume agricultural wastes as value-added raw materials.

Results and Discussion

Biomass Solubility Assessments

Cascara was explored as a source for ionic liquid (IL) mediated cellulose extraction using [DBUH][OAc]. The solubility of unprocessed cascara was investigated for a range of biomass loadings (3-15% w/w). It was found that cascara is only partially soluble in [DBUH][OAc], with only 65 ± 1% of initially input biomass dissolving within 4 hours at 80° C. In comparison, the cotton control was 100% soluble in [DBUH]OAc] at 3-15% loading under the same conditions. **Figure 1** shows a correlation between the amount of biomass added and the effective dissolution amount. There is a strong linear relationship showing a consistent solubility of cascara in [DBUH][OAc], with some deviation starting at 15% cascara loading. The reduction in functional dissolution at 15% suggests that either a saturation limit has been reached, or a critical viscosity has been achieved that kinetically limits further dissolution.[19,38,41] A substantial mass of insoluble, undissolved material (UDM) remained even at low concentrations of cascara (<1% w/w), suggesting strong intramolecular bonding within the lignocellulosic matrix[42] even after 4 hours of heating.

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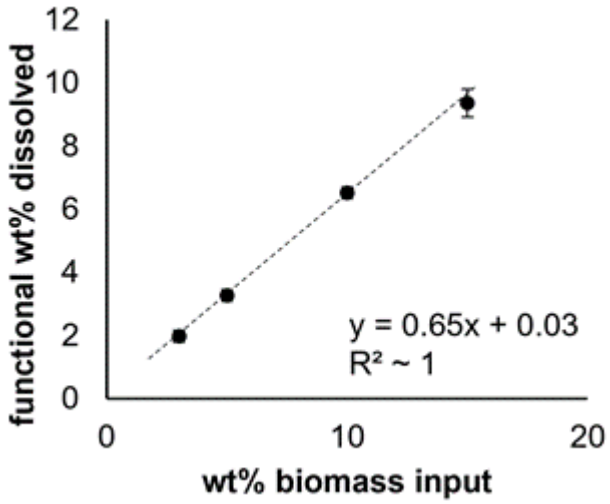

Figure 1. Dissolution efficiency of dry cascara biomass in [DBUH][OAc] IL (3,5,10,15 % w/w) after 4h of heating at 80° C

Biomass Compositional Assessments

We assessed whether there were any differences between the untreated cascara, precipitated films, and UDM. Initially, it was thought that the dissolved fraction was composed largely of cellulose, because the measured 65% dissolution rate corresponds well with Murthy and Naidu's measurement of 63% cellulose content in cascara.[29] However, measurement using the NREL protocols for cellulose, hemicellulose, acid-soluble lignin, and acid-insoluble lignin suggests that [DBUH][OAc] solvation is not selective for cellulose alone **(Table 2)**. The cascara purchased from the De La Gente Cooperative in Guatemala contains substantially less cellulose by mass percent than measured by Murthy and Naidu although they may have assessed a different coffee cultivar.[29] When normalized to consider exclusively the structural lignocellulosic biomass components, the untreated cascara is 24% cellulose and 62% total lignin compared to 38% and 52% respectively in the precipitated cascara films. The hemicellulose content remains relatively unchanged between the untreated cascara, precipitated film, and the undissolved material. Comparison of the UDM to the untreated coffee fruit shows limited difference beyond a slight increase in acid soluble lignin which appears to be minimally soluble in [DBUH][OAc]. The high cellulose content in the UDM suggests that further dissolution optimization could be achieved under different conditions. A large mass of extracts was also conveyed in the [DBUH][OAc], which along with the lignin and hemicellulose content interrupt cellulose crystallization on re-coagulation **(Figure 2)**. In future work we will assess the impacts of pretreatments that reduce how much lignin, lipids, proteins, and non-structural sugars are available when separations are performed using ionic liquids.

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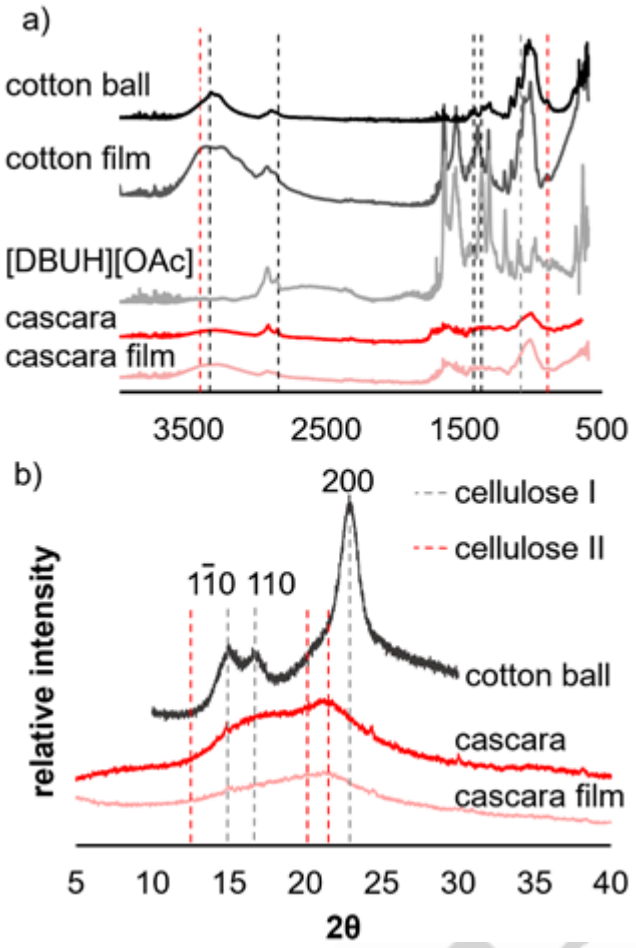

Figure 2. analysis of native biomass and precipitated biomass films using a) FTIR in absorbance mode and b) XRD. Dashed lines indicate expected peak positions of Cellulose I (black) and Cellulose II (red).

Comparisons were also performed using XRD and FTIR to assess the crystallinity of native biomass and precipitated films (**Figure 2**). Cotton extracted from cotton balls is highly pure cellulose I as demonstrated by characteristic XRD diffraction peaks at 15.1°, 16.6°, ad 22.8° corresponding to the [1-10], [110], and [200] diffraction lines of Cellulose I.[43] The determination of cellulose crystals in cascara was more ambiguous. The native cascara FTIR scan confirms the characteristic bond absorptions in cellulose,[44,45] but there was extensive peak broadening in the XRD, and peaks were shifted from the usual cellulose I or II peaks.[43] The native cascara is more crystalline than the precipitated cascara film, which shows a larger amorphous halo in the XRD diffraction[45,46] and the absence of a shoulder at 1090 cm^{-1} (and 1111 cm^{-1} in Cellulose I) in the FTIR scan (**Figure 2a)** which is linked with both the cellulose I and cellulose II crystal structures.[44,47] A cotton film precipitated into antisolvent from [DBUH][OAc] was also assessed and identified as cellulose II based on FTIR peaks at 893 cm^{-1} and 3414 cm^{-1}, and the loss of peaks at 1375 cm^{-1}, 1430 cm^{-1}, and 3345 cm^{-1}. [48,49] The cotton film also retained some IL content, indicated by shared peaks between the cotton film and the spectra for [DBUH][OAc], which was not present in cascara films. The IL also appeared to plasticize the cotton film yielding a rubbery transparent film.

Rheological Analysis

Rheological analysis was performed to assess how increased amounts of biomass loading affected the IL solution behavior comparing cascara with a cotton control. Comparison of complex melt viscosity at elevated temperature for a range of biomass concentrations is presented in **Figure 3a,b**. Both cascara and the cotton/IL solutions experience a rise in viscosity with increasing biomass loading and show characteristic shear thinning at higher shear rates, as expected.

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The solutions were assumed to fit the Cox-Merz rule,[50,51] and zero shear values were calculated using both Newtonian plateau determination and the Carreau model fitting (**Table 3**).

The cotton/IL solutions are much more viscous compared to equivalent concentrations of the cascara biomass evaluated under the same conditions. The lower viscosity of cascara solutions is likely a result of the presence of lignin and small molecule impurities like sugars and pigments that convey in the IL, as well as the presence of small UDM particulate matter. Silva and Byrne observed a similar gap in Newtonian plateau magnitude between cotton with degrees of polymerization (DP) 2680 and 495 dissolved in [AMIM][Cl][37], although this is inconclusive to determining the DP of cellulose in cascara. Zero shear viscosities were calculated (n = 3) using Newtonian plateau estimations for dilute biomass solutions, and curve fitting of the Cross and Carreau models for more concentrated solutions **(Table 3, SI)**.[50,51] The Cross and Carreau models describe the non-Newtonian shear-thinning behavior of polymers.[50,51] The Carreau model **(Eqn 1)** was found to fit the cascara better than the Cross model **(SI)** and is presented in **Table 3**.

$$\eta(\dot{\gamma}) = \eta_0(1 + (\tau\dot{\gamma})^2)^{\frac{(n-1)}{2}} \qquad \text{Eqn 1}$$

Where η_0 is the zero shear viscosity, τ is a time constant, and n is the power-law exponent. The zero shear viscosity behavior of the cascara solutions tracked similarly with zero shear curves of 265 DP micro crystalline cellulose in [DBUH][Prop][48] and poplar woody biomass in [Emim][OAc][36] **(Figure 4)**.

Table 2. Compositional assessment of biomasses

Sample	Cellulose (%)	Hemicellulose (%)	Acid Soluble Lignin (%)	Acid Insoluble Lignin (%)	Extracts[a] (%)
Untreated cascara	12.83 ± 0.01	7.10 ± 0.10	10.65 ± 0.40	21.9 ± 0.30	47.53 ± 0.80
Cascara film[b]	26.50	7.33	8.1	28.8	29.27
UDM	13.54 ± 0.10	5.60 ± 0.02	13.3 ± 0.01	20.05 ± 0.40	47.52 ± 0.52
Cotton	100 ± 3.92	-	2.61 ± 0.29	-	-

[a] Including lipids, proteins, non-structural sugars, and small molecule compounds. [b] An individual sample was characterized for films; all others were performed in duplicate.

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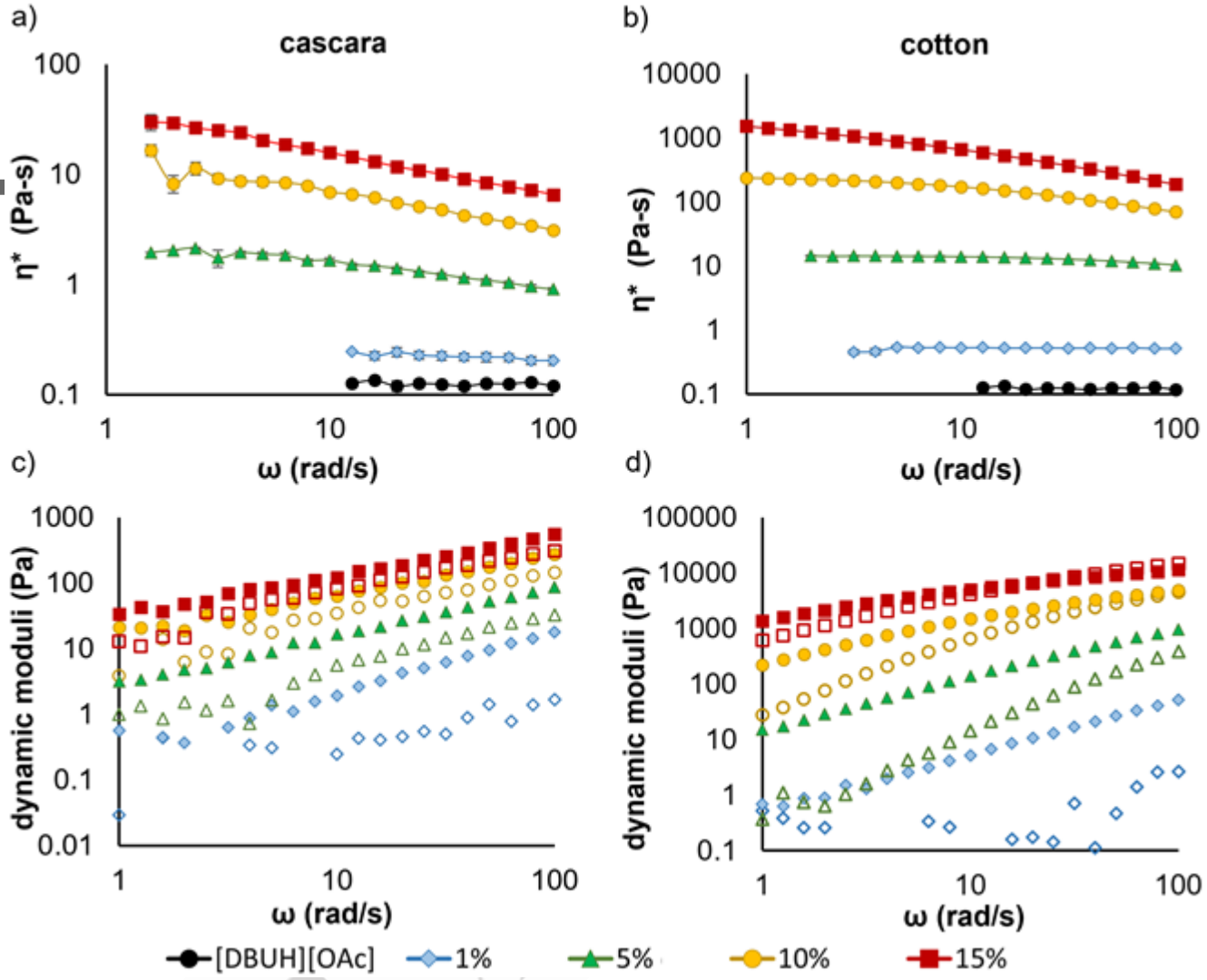

Figure 3. Concentration dependent rheology data, complex viscosities of cascara (a) and cotton (b), and storage (G') and loss moduli (G") for cascara (c) and cotton (d) where closed symbols are G" and open symbols are G.

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Table 3. Zero shear values (η_0) and Carreau parameters for cotton and cascara at 60°C

Conc.	η_0 (Pa.s)	t	n
0[b]	0.13± 0.00	-	-
1[b]	0.53 ± 0.01	-	-
5	14.4 ± 0.1	0.045 ± 0.00	0.79 ± 0.00
10	232 ± 2	0.21 ± 0.01	0.63 ± 0.01
15	1510 ± 40	0.55 ± 0.04	0.50 ± 0.01
Conc.	**η_0 (Pa.s)**	**t**	**n**
0[b]	0.13 ± 0.00	-	-
1[b]	0.22 ± 0.01	-	-
5	2.29 ± 0.15	0.43 ± 0.15	0.76 ± 0.01
10	9.97 ± 0.30	0.22 ± 0.02	0.62 ± 0.01
15	43.0 ± 6.3	1.27 ± 0.43	0.60 ± 0.00

[a] error reported as 1 standard deviation.

[b] Determined from Newtonian plateau estimation.

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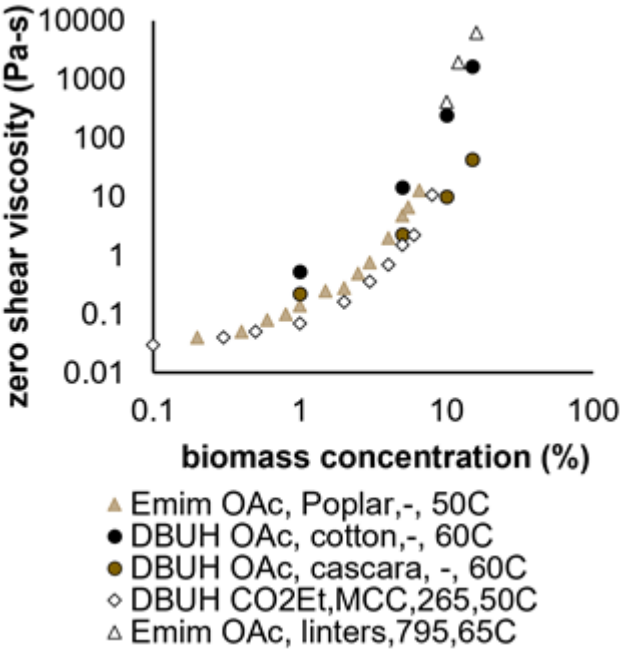

Figure 4. Comparison of concentration dependent h_0 values for a range of biomasses, ionic liquids, and temperatures including our data on cascara and cotton. Data IDs are presented as IL, biomass, molecular weight, temperature[36,48,52].

The storage (G") and loss (G') moduli of the cotton and cascara were also measured at 60°C (**Figure 3c,d)**. As seen in **Figure 3c,d**, G" is greater than G' in the measured range for all observed concentrations of cascara, although G' converges towards G" with increasing cascara concentration. The cotton solutions demonstrate similar behavior, with solutions below 10% having a more fluid-like behavior up to 100 rad s^{-1}. At 10% cotton loading, the crossover point (COP) is approached, and at 15% the COP occurs at 6900 ± 60 Pa and 20 ± 1 rad s^{-1}. The COP is interpreted as being due to molecular entanglements and the cohesiveness of polymer solutions which influence fiber drawing.[53] Lower temperatures would induce the COP at lower angular frequency in both the higher concentration cotton and cascara solutions. Sixta and coworkers identified a narrow window of COPs that promoted high draw ratios during fiber spinning with ranges between 0.6–1.2 s^{-1} and around 3.7–5.8 kPa.[11] Although high draw ratios, defined as the ratio of the rate of fiber extension to extrusion in industrial fiber spinning have been correlated with better fiber properties,[11,54] low draw ratios can still generate fibers when solutions are sufficiently cohesive.[53]

Coagulated Product Formation

Fibers were pulled by hand in the biomass/IL gel state and coagulated in a room temperature water bath. Fiber dimensions were controlled by the amount of biomass solution used and the degree to which it was drawn. Using the present method, fibers as long as 5 cm could consistently be produced.

The ability to draw cohesive fibers was strongly impacted by the concentration of biomass in solution. Viable, precipitated fibers were drawn from cotton/IL solutions at 70°C with loadings as low as 3% w/w whereas cascara solutions required loadings of 8% and higher to yield cohesive fibers. The biomass loading and the quality of the biomass influence both the viscosity and the cohesiveness of the solution.[56] At 5% cascara in IL solutions, adding biomass solution to the coagulation bath resulted in nearly complete cohesive failure of fibers as IL was removed likely due to insufficient cellulose-cellulose bonds resulting from elevated levels of lignin and extracts presence. We also postulate that the cellulose in cascara is of lower molecular weight than that of the cotton, which would also add to the lower cohesive strength of dilute cascara solutions. A minimum number of polymer chain-chain interactions is required for the biomass solution to condense into a solid when the IL is washed away, with longer cellulose chains requiring fewer strands to achieve that threshold.[48]

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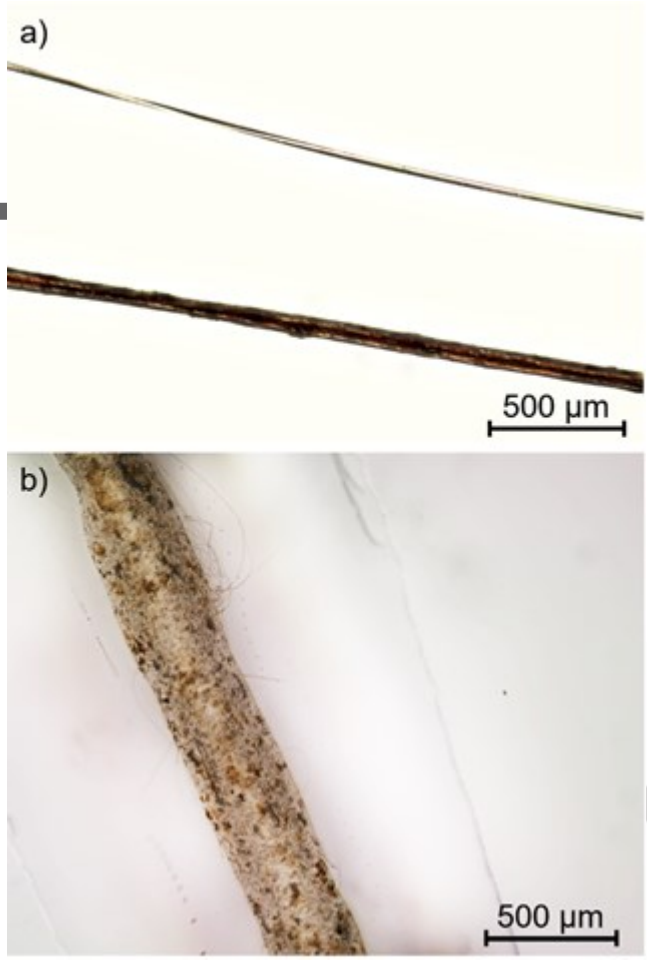

Figure 5. Optical image depicting hand drawn fibers. a) cotton derived fiber (top) and a cascara fiber (bottom) both from 10% w/w solutions. b) a cascara fiber swelled with water. Speckles are indicative of UDM.

As the hand drawing technique was being optimized, fibers of varying thickness were made from both cotton/IL and cascara/IL solutions, which were then measured using optical microscopy **(Figure 5)**. Fibers ranging in diameter from several hundred microns down to below 30 µm could be produced. The finest fibers had diameters of 26 ± 4 µm and 18 ± 1 µm respectively for cotton and cascara. Fiber diameters varied between 5 and 15% over their length. It is likely that thinner and more consistent fibers could be produced through automation,[14] as the current manual process is limited by technician skill. The ability to manually produce fibers on the diameter scale of commercially relevant fibers[57] suggests promise for the valorization of cascara biomass despite the high concentration of non-cellulose compounds.

Cascara derived fibers had a brown pigmentation due to the high lignin concentration and retention of natural pigments. Small fractions of undissolved material (UDM) were also retained in the cascara derived fibers and films **(Figure 5b, 6b)**. Fibril and film mechanical behavior were not assessed here, and offers area for future work, along with purifying cascara residues.

Films were also made from 10% cascara/IL solution by coagulation of the cellulose rich solutions in methanol. The low vapor pressure of methanol allowed for easier solvent recovery through rotary evaporation and subsequent recycling in film coagulation baths. Films of varying sizes were made by applying uniform layers of cascara/IL solution to glass

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substrates for subsequent coagulation in an antisolvent bath. Small films were made using borosilicate microscope slides, and larger films were made by applying solution to the external surface of 250 mL glass beakers as substrates for coagulation. **Figure 6a** shows examples of films produced on microscope slides. Unlike with biomass fibers, coagulated films were dried on a flat surface under compression. Films left to dry uncompressed warped due to uneven lateral shrinkage. The films were observed with optical microscope and SEM. Analysis of the topography of the films with SEM showed that the surface structure of the films **(Figure 6c)** is very similar to the surface of the dehydrated coffee fruit **(Figure 6d)**.

We continue to optimize film making conditions to make more robust samples to quantify the strength and stiffness of precipitated cascara and cotton. We are also resolving ways to manipulate the solvation capacity of the IL for better separations of lignin and cellulose fractions to yield purer starting material. The current efforts demonstrate the viability of cascara as a value-added feedstock for man-made fibers as well as a possible source of lignin. Future work will look at pretreatments to isolate the cellulosic fraction of cascara as well as the recovery of the ionic liquid fraction from the coagulation bath. Although these preliminary fibers derived from hand-drawn cascara are inferior to native cotton, there might be many other uses for these derivative forms as-is beyond structural applications.

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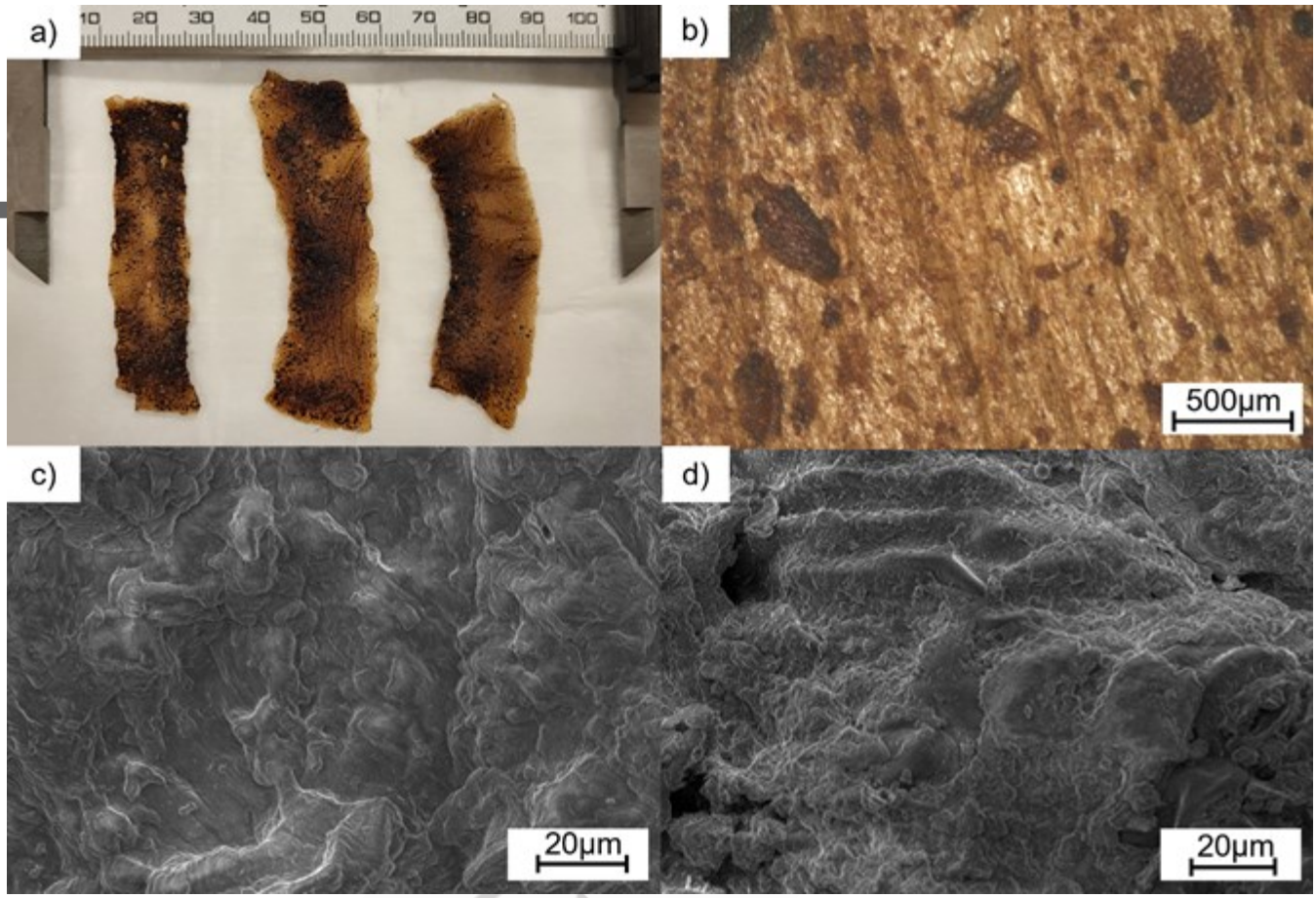

Figure 6. Images of films produced from 10% cascara solutions. A) full sized films, b) optical microscope image of a film showing embedded particulates, c) SEM image of a film, d) SEM image of an unprocessed cascara fruit

Conclusion

Native coffee fruit (cascara) and cotton were dissolved in [DBUH][OAc] ionic liquid and probed as sources of lignocellulosic feedstocks for producing fibers and films. Material balances of the IL solutions and the precipitates produced by exposure to both methanol and DI water antisolvents were characterized and analyzed for cellulose crystallinity and lignin (acid soluble and insoluble). Coffee fruit was found to be ~65% soluble in [DBUH][OAc] at 80°C. Comparing the measured zero shear viscosity trends with those in the literature shows that the cascara solutions perform similarly to low molecular weight microcrystalline cellulose and poplar woody biomasses. Procedures were developed in which the soluble fraction could be spread or stretched and deposited into a coagulation bath allowing for the precipitation of films and fibers as fine as 30 µm in diameter. Fibers were produced from both coffee fruit and cotton although they are both structurally inferior to native cotton. The capacity to produce fibers and films from IL solutions offers a promising proof of concept but there is a lot of work that is still needed to pretreat the biomass to isolate sugars and other non-structural elements before exposing the biomass to ionic liquids for biopolymer isolation. And finally, rheological analysis of the cascara solutions suggests that the unpurified solutions are not optimized for higher throughput fiber spinning. Further work is underway to assess the application of ionic liquid pretreatments and dilute acid pretreatments to cascara biomass. Altogether, preliminary assessment of coffee fruit as a value-added feedstock for cellulose and lignin seems promising. Efforts to develop schemes to fractionate cellulose and lignin rich residues in a more contained system open the possibility to leverage complex biomasses like cascara.

Supporting Information

The authors have cited additional references within the Supporting Information[58-61].

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Acknowledgements

Funding acknowledgement: JMR acknowledges the support of the PPG Foundation for fellowship support. Acknowledgements are also in order for Thomas Marks for providing insight on statistical analysis and code development as well as Dr. Shireesh Srivastava and Professor Eric Hegg for providing biomass characterization. And finally to the staff and facilities of the University of Michigan VanVlack Laboratory.

Keywords: Biomass • Ionic liquids • Cellulose • Cascara • Renewable resources

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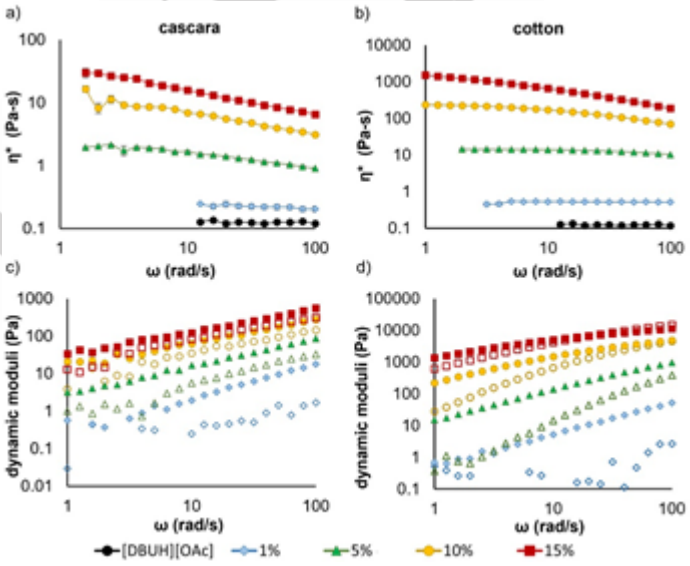

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This paper considers the use of ionic liquids as solvents to fractionate coffee fruit discards called cascara for subsequent fiber and biopolymer isolation. The team probes overall solubility characteristics comparing coffee residues with cotton and analyzes the composition and properties of the precipitates that are produced.

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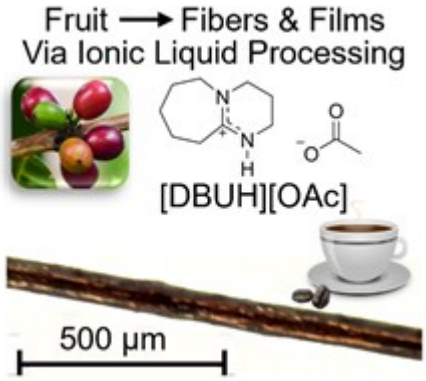

Coffee fruit is a high-volume agriculture waste rich in cellulose and lignin that is environmentally and economically expensive to dispose of. Herein ionic liquids are applied to dissolve and shape coffee fruit to yield proof-of-concept fibers and films.

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